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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

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Modified supported metallocene catalysts for the polymerization of olefins

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Modified Supported Metallocene Catalysts for the Polymerization of Olefins

The invention relates to modified supported metallocene catalysts for the polymerization of olefins, based on inorganic oxides and metallocenes.

Metallocenes of the metals of e.g. transition group IV of the Periodic Table of the Elements are highly active catalysts for the polymerization of olefins. The resulting polyolefins have new advantageous combinations and supplement the product range of the polyolefins prepared hitherto using known conventional Ziegler-Natta catalysts.

It is known that catalysts based on unbridged, substituted and unsubstituted biscyclopentadienyl metallocenes in combination with aluminoxanes as cocatalyst can be used for the preparation of polyethylene and ethylene-olefin copolymers (EP 0 128 046).

It is also known that stereoregular polyolefins can be prepared using bridged, chiral metallocenes. For bridging the ligand systems, use is mostly made of dimethylsilane-diyl groups (EP 0 316 155), methylphenylsilanediyl groups (EP 0 320 762), ethylene groups (Brintzinger, J. Organomet. Chem. 288 (1985), 63-67) isopropylidene bridges (EP 0 459 264) and silyl-substituted diyl bridges (WO 97 02 276).

Depending on the ligand type and the substituents, isotactic, syndiotactic, hemi-isotactic, stereoblock-type and atactic homopolymers and copolymers having aliphatic or cyclic structures can be prepared.

As ligands, preference is given to using substituted and unsubstituted cyclopentadienyl units (EP 316 155), substituted and unsubstituted indenyl units (EP 0

302 424; EP 0 485 823) and also substituted and unsubstituted cyclopentadienyl units in combination with unsubstituted fluorenyl groups (EP 0 412 416).

It is further known that bridged metallocenes having a cyclopentadienyl system and a heteroatom ligand (constrained geometry catalyst) can also be used for the polymerization of olefins (US 5 096 867).

A disadvantage of such homogeneous catalysts in the polymerization of olefins are the resulting powders, having only a low bulk density. The particle morphology of such products can in principle be somewhat improved by a specific pretreatment of the metallocene with the cocatalyst (EP 0 302 424). However, such a process has the disadvantage of, in particular, heavy deposit formation in industrial reactors (EP 0 563 917).

Although the use of methylaluminoxane, which is insoluble in aliphatic solvents, as support material gives a certain improvement in the activity and likewise leads to pulverulent products [Polymer 32(1991), 2671-2673].

Supporting the metallocene on oxidic materials such as silicon oxide or aluminium oxide with pretreatment of the starting material, which may be partially dehydrated, with the cocatalyst is a known method (WO 91 09 882) used in homopolymerization and copolymerization of ethylene. However, in this method, the particle size of the polymer particle is determined essentially by the particle size of the support material.

Further processes describe the modification of the oxidic support using methylaluminoxanes and the subsequent application of the metallocene (EP 0 206 794). However, this method restricts the ability to control the particle size by means of the properties of the support materials.

EP 0 685 494 describes a further supported catalyst which is prepared by the application of methylaluminoxane to a hydrophilic oxide, subsequent crosslinking of the methylaluminoxane using a polyfunctional organic crosslinker and subsequent application of an activated methylaluminoxane/metallocene complex. The disadvantage of this supported catalyst is that at the relatively high polymerization conversions achieved in industrial plants, the strength of the supported catalysts is not sufficient to ensure a compact, granular morphology of the polymer product.

A support material by drying hydrophilic inorganic oxides and reacting with aluminoxanes and polyfunctional crosslinkers gives, after contacting with catalysts, a supported catalyst system for a stable high bulk density in olefin polymerization even at high conversion rates (EP 0 787 746).

Methods for modifying homogeneous catalysts and supported catalyst systems by pre-polymerization are also known.

In EP 0 354 893 a homogeneous catalyst is prepared by pre-polymerizing a precipitated complex of an aluminium alkyl and a metallocene catalyst with an olefin monomer at a temperature below the polymerization temperature of the monomer, followed by polymerizing the olefin monomer under polymerization conditions. EP 0 426 638 describes the pre-polymerization of propylene in combination with homogeneous metallocene catalysts for reproducible and controllable polymerization. The disadvantage of homogeneous polymerization, resulting in powders having only a low bulk density, is not resolved in these processes.

For supported catalyst systems, pre-polymerization of olefinic monomers is known from EP 0 705 281 using bis-indenyl metallocene reaction product catalysts whereby the indenyl rings are 2-substituted, further from WO 97 02 297 wherein the pores of the catalyst system contain a volume of liquid that is equal

to or less than the total pore volume of the supported catalyst system. In WO 96 28 479, a supported metallocene catalyst system having an activity greater than 100,000 g/g/h and at least an α -olefin monomer are combined under pre-polymerization conditions, hydrogen is added, and after recovering the pre-polymerized supported catalyst system, ethylene or propylene is fed for polymerization.

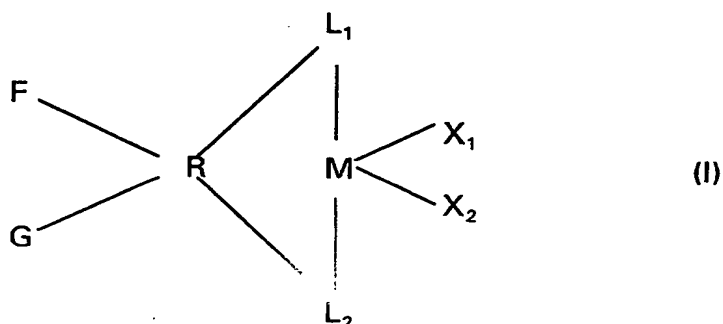
One of the main disadvantages of these known pre-polymerization processes is the impossibility to use the known metallocene supported catalysts necessary for the production of high molecular weight polyolefins without reactor fouling, formation of polymer fines resulting from soluble catalyst components and disrupted catalyst components in the initial phase of the olefin polymerization under technical liquid olefin polymerization conditions.

It is therefore an object of the invention to find a supported metallocene catalyst for liquid-phase polymerization of olefins for the production of high molecular weight polyolefins without reactor fouling, formation of polymer fines resulting from soluble catalyst components and disrupted catalyst components in the initial phase of the olefin polymerization.

It has now surprisingly been found, that these requirements are achieved by a modified supported metallocene catalyst for olefin polymerization, especially for liquid-phase polymerization of olefins, comprising

A) 90.0 – 99.9 parts by weight of a catalyst support based on a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof, which catalyst support is obtainable by simultaneous reaction with aluminoxanes and with polyfunctional organic crosslinkers,

B) 10 – 0.1 parts by weight of a metallocene compound of the formula I



where

M is a metal selected from the group consisting of Ti, Zr, Hf, V, Nb and Ta or an element selected from the group consisting of the lanthanides,

X₁ and X₂ are identical or different and are each a C₁-C₁₀-alkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₂₀-alkylaryl group, a C₇-C₂₀-arylalkyl group, a C₈-C₂₀-arylalkenyl group, hydrogen or a halogen atom,

L₁ and L₂ are identical or different and are each an unsubstituted, monosubstituted or polysubstituted monocyclic or polycyclic hydrocarbon radical containing at least one cyclopentadienyl unit which can form a sandwich structure with M, R is carbon, silicon, germanium or tin,

F and G are identical or different and are each a trimethylsilyl radical of the formula -Si(CH₃)₃, where G may also be a C₁-C₁₀-alkyl radical, preferably a C₁-C₄-alkyl radical, or a C₆-C₁₀-aryl radical,

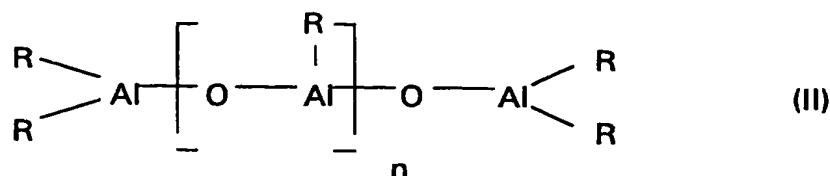
whereby according to the invention said supported metallocene catalyst comprising the catalyst support A and the metallocene B has an activity of maximum 100 kg, preferably maximum 50 kg, particularly preferred maximum 20 kg polyolefin/g supported catalyst/h and is modified by pre-polymerization with an

olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization, resulting in 0.01 – 1.0 parts by weight, relative to A + B, of a polyolefin or olefin copolymer C), different to the polyolefin or olefin copolymer from the subsequent olefin polymerization or olefin copolymerization, and whereby the melting point or softening point of the polyolefin or olefin copolymer C) resulting from pre-polymerization is at least 20 °C higher, preferably 30 °C or 50 °C higher than the melting point or softening point of the polyolefin or olefin copolymer, resulting from the subsequent olefin polymerization or olefin copolymerization under application of said modified supported metallocene catalyst. It is also possible that the supported metallocene catalyst has an activity of maximum 5 kg or maximum 10 kg polyolefin/g supported catalyst/h.

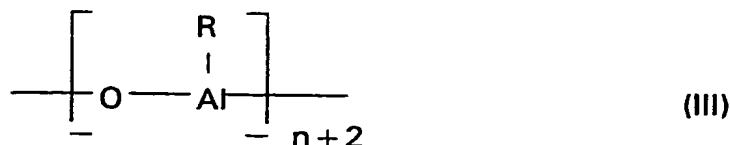
The hydrophilic oxides used in the catalyst support A) usually contain hydroxyl-groups and/or physically absorbed water. They are preferably porous and finely divided and usually have a mean particle size of from 10 to 300 microns.

Preferably the hydrophilic inorganic oxide in the catalyst support A) is an aluminum oxide (alumina), silicon oxide (silica), magnesium oxide, titanium oxide or zirconium oxide or a mixture or mixed oxide thereof. Particular preference is given to using silicon dioxides of the Grace Davison type. However, other suitable starting materials are finely divided oxides, for example those described in EP 0 585 544, which are prepared by high temperature hydrolysis from gaseous metal chlorides or silicon compounds.

According to the present invention, the aluminoxane used in the catalyst support A) is a linear aluminoxane of the formula II



or an aluminoxane of the cyclic type III



where, in the formula II and III, the radicals R can be identical or different and are each a $\text{C}_1\text{--C}_6$ -alkyl group and n is an integer in the range 1 - 50. Preferably, the radicals R are identical and are methyl, isobutyl, phenyl or benzyl. The aluminoxane can be prepared in various ways by known methods. One possibility is, for example, the reaction of aluminium alkyls with aluminium sulphate containing one water of crystallisation (EP 0 302 424).

In the catalyst support A), the molar ratio of aluminium (as aluminoxane) to surface hydroxyl groups of the hydrophilic inorganic oxide is between 1 and 50, preferably between 1 and 30.

According to the invention, suitable polyfunctional organic crosslinkers in the catalyst support A) are all inorganic compounds having more than one functional group which can react with metal-carbon bond. Preference is given to using a bifunctional crosslinker. Such bifunctional organic compounds can be, for example, aliphatic or aromatic diols, aldehydes, dicarboxylic acids, primary or secondary diamines, diepoxy compounds. Most preference is given to using aliphatic and aromatic diols, secondary amines or diepoxy compounds or mixtures thereof. Particular preference is given to using ethylene glycol, butanediol, bisphenol A and 1,4-butanediol diglycidyl ether. Tri- or higher functional crosslinkers which can be used are, for example, triethanolamine, glycerol, phloroglucinol or tetraethylenepentamine.

The molar ratio between the aluminium as aluminosilicate and the polyfunctional organic compound in the catalyst support can vary within a wide range and is between 1 and 100, preferably between 1 and 40. Higher molar-ratios of aluminium to polyfunctional organic compound are used particularly when use is made of tri- or higher-functional crosslinkers which can form a correspondingly higher number of crosslinks.

According to the invention, preferred ligands L_1 and/or L_2 in the metallocene compound B) are substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl radicals. Particular preference is given to cyclopentadienyl, tetramethylcyclopentadienyl, indenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, 2-methyl-4,5-benzindenyl and fluorenyl units and also ferrocene- and ruthenocene-substituted units as are described, for example, in EP 0 673 946.

According to the invention, the following metallocenes are particularly preferred :

bis-(trimethylsilyl) silanediylidicyclopentadienylzirconium dichloride,

bis (trimethylsilyl) silanediylindenylzirconium dichloride,

bis (trimethylsilyl) silanediylbis (2-methylindenyl) zirconium dichloride,

bis (trimethylsilyl) silanediylbis (2-methyl-4,5-benzindenyl) zirconium dichloride,

bis (trimethylsilyl) silanediylbis (2-methyl-4-phenylindenyl) zirconium dichloride,

bis (trimethylsilyl) silanediylbis (2-methyl-4-naphthylindenyl) zirconium dichloride,

bis (trimethylsilyl) silanediyl difluorenylzirconium dichloride,

bis-(trimethylsilyl) silanediyl (fluorenyl) (cyclopentadienyl) zirconium dichloride,

bis (trimethylsilyl) silanediyl (fluorenyl) (indenyl) zirconium dichloride,

bis (trimethylsilyl) silanediyl (tetramethylcyclopentadienyl) (indenyl) zirconium dichloride,

methyl (trimethylsilyl) silanediylidicyclopentadienylzirconium dichloride,

methyl (trimethylsilyl) silanediylindenylzirconium dichloride,

methyl (trimethylsilyl) silanediylbis (2-methylindenyl) zirconium dichloride,

methyl (trimethylsilyl) silanediylbis (2-methyl-4,5-benzoindenyl) zirconium dichloride,

methyl (trimethylsilyl) silanediylbis (2-methyl-4-phenylindenyl) zirconium dichloride,

methyl (trimethylsilyl) silanediylbis (2-methyl-4-naphthylindenyl) zirconium dichloride,

methyl (trimethylsilyl) silanediyl difluorenyl zirconium dichloride,

methyl (trimethylsilyl) silanediyl (fluorenyl) (cyclopentadienyl) zirconium dichloride,

methyl (trimethylsilyl) silanediyl (fluorenyl) (indenyl) zirconium dichloride and

methyl (trimethylsilyl) silanediyl (tetramethylcyclopentadienyl) (indenyl) zirconium dichloride.

According to the invention, in the metallocene compound B) in addition also amido, phosphido and arsenido radicals can be used as ligands L_2 , where the substituents of these ligands are as defined for X_1 and X_2 , or substituted or fused ferrocenyl- or ruthenocenyl-radicals.

According to the invention, preferably the olefin or an olefin mixture used in the modification of the supported metallocene catalyst by pre-polymerization, resulting an polyolefin or olefin copolymer C), is 3-methylbutene-1, 4-methylhexene-1, 4-methylpentene-1, vinylcyclohexane, vinylcyclopentane and/or vinylcyclopropane.

The invention further provides a process for preparing a modified supported metallocene catalyst for polymerization of olefins, especially in liquid phase, comprising the steps:

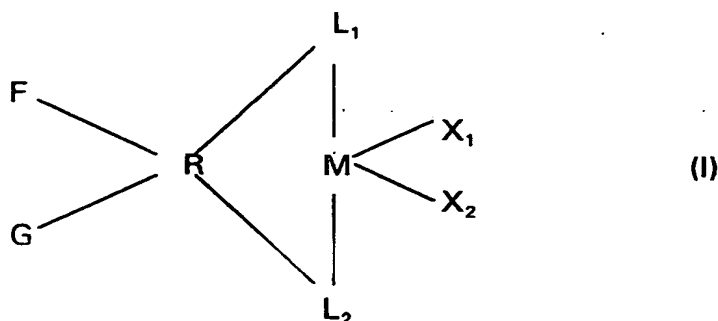
α) preparing a catalyst support A) by

α 1) drying a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof at from 110 to 800°C, subsequently

α 2) if desired, reacting the free hydroxyl groups of the oxide completely or partially with aluminoxanes or aluminium alkyls and subsequently

α 3) reacting the oxide simultaneously with aluminoxanes and polyfunctional organic crosslinkers,

β) suspending the catalyst support A) in an inert hydrocarbon and bringing it in contact with a solution of a metallocene compound B) of the formula I in an inert hydrocarbon, wherein 90.0 – 99.9 parts by weight of a catalyst support A) are mixed with 10 – 0.1 parts by weight of the metallocene compound B)



where

M is a metal selected from the group consisting of Ti, Zr, Hf, V, Nb and Ta or an element selected from the group consisting of the lanthanides,

X_1 and X_2 are identical or different and are each a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -alkoxy group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{20} -alkylaryl group, a C_7 - C_{20} -arylalkyl group, a C_8 - C_{20} -arylalkenyl group, hydrogen or a halogen atom,

L_1 and L_2 are identical or different and are each an unsubstituted, monosubstituted or polysubstituted monocyclic or polycyclic hydrocarbon radical containing at least one cyclopentadienyl unit which can form a sandwich structure with M, R is carbon, silicon, germanium or tin,

F and G are identical or different and are each a trimethylsilyl radical of the formula $-\text{Si}(\text{CH}_3)_3$, where G may also be a C_1 - C_{10} -alkyl radical, preferably a C_1 - C_4 -alkyl radical, or a C_6 - C_{10} -aryl radical,

γ) modifying said supported metallocene catalyst, which has an activity of maximum 100 kg, preferably maximum 50 kg, particularly preferred maximum 20 kg polyolefin/g supported catalyst/h, by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization, resulting in 0.01 – 1.0 parts by weight, relative to the sum of the weight of the catalyst support and the metallocene compound, of a polyolefin or olefin copolymer C), different to the polyolefin or olefin copolymer from the subsequent olefin polymerization or olefin copolymerization, and whereby the melting point or softening point of the polyolefin or olefin copolymer C) resulting from pre-polymerization is at least 20 °C higher, preferably 30 °C or 50 °C higher than the melting point or softening point of the polyolefin or olefin copolymer, resulting from the subsequent olefin polymerization or olefin copolymerization under application of said modified supported metallocene catalyst.

—In the first stage α1), the oxide is preferably dehydrated in a stream of nitrogen or under reduced pressure at temperatures of from 110 to 800°C over a period from 1 to 24 hours. The concentration of free hydroxyl groups, established as a function of the drying temperature selected, is then measured. The free hydroxyl groups can be reacted completely or partially with aluminoxanes or aluminium alkyls in stage α2).

In stage $\alpha 3$), the dried oxide is reacted simultaneously with aluminoxanes and at least one polyfunctional organic crosslinker, which is suspended, for example, in a suitable hydrocarbon solvent such as toluene in such a way that it is covered with the solvent. The solvents for the aluminoxane and for the crosslinker have to be miscible and the same solvents are preferable used. Particular preference is given to using toluene.

In the preparation of the catalyst support A), the molar ratio of aluminium (as aluminoxane) to the surface hydroxyl groups of the hydrophilic inorganic oxide is, e.g. between 1 and 50, preferably between 1 and 30, particularly preferably between 5 and 20.

To prepare the solution needed in stage $\alpha 3$), the solvent used for the crosslinker can be the same as for the aluminoxane solution. Owing to the temperature dependence of the solubility of these crosslinkers in the solvent used, the desired concentration can be set in a targeted manner by the choice of the temperature of the solution. Particularly advantageous is the selection of a solvent whose boiling point is below the decomposition temperature of the solid prepared in stage $\alpha 3$). Preference is given to using aromatic solvents such as xylene, benzene or toluene.

When using the polyfunctional crosslinkers in preparing the catalyst support in stage $\alpha 3$), it is also possible, in a further reaction stage, to deactivate unreacted reactive groups using, for example, alkylaluminium compounds, preferably using trimethylaluminium.

The molar ratio between the aluminium used in stage $\alpha 3$) as aluminoxane and the crosslinker can vary within a wide range and is between 1 and 100, preferably between 1 and 40, particularly preferably between 10 and 25. It is depend-

ent, in particular, on the type and pretreatment of the metal oxides, the type of aluminosilicates used, on the respective molar ratio of aluminium (as aluminosilicate) to the surface hydroxyl groups on the metal oxide and on the type of crosslinker. Higher molar ratios of aluminium to the crosslinker are used particularly when use is made of tri- or higher functional crosslinkers which can form a correspondingly higher number of crosslinks.

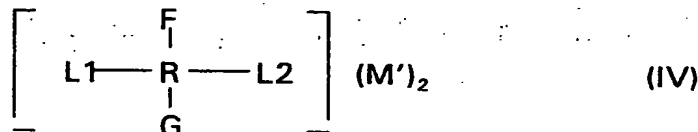
The suspended dried oxide from stage $\alpha 1$) is preferably treated with a solution of aluminosilicate and a solution of one or more polyfunctional organic crosslinkers in the same solvent. If desired, it is also possible in stage $\alpha 2$) to react the free hydroxyl groups of the oxide with an up to equimolar amount of an aluminosilicate or an aluminium alkyl solution, for example trimethylaluminium, prior to the crosslinking reaction. Preference is given to using methylaluminosilicate for this purpose. It has been found to be particularly advantageous if all hydroxyl groups have been reacted. However, even a partial reaction of these groups gives a positive effect.

According to the invention, in stage $\alpha 3$) for preparing the catalyst support, the metering in of the solutions is carried out simultaneously and continuously and the crosslinker solution may be heated or cooled if desired. The temperature to which the solution is heated or cooled depends on the solubility of the crosslinker in the solvent selected and on the desired crosslinking density on the support surface. The rate at which the two streams are metered in can be set by means of metering pumps and is in a range between 0.1 and 1000 ml per minute, preferably between 0.5 and 250 ml per minute, particularly preferably between 1 and 50 ml per minute. The reaction is preferably carried out in such a way that all the aluminosilicate has been reacted after the simultaneous metering in of the two solutions. Under some circumstances, fluctuations in the reaction conditions on the industrial scale can lead to unreacted aluminosilicate remaining in the solution. The usable catalyst supports as described in EP 0 685 494

display a soluble aluminium proportion in the solvent used of preferably less than 1.4 mol% based on the aluminosilicate used. In this case, it is possible to carry out one or more washing steps in order to reduce the concentration below the desired limit. It is also possible to add a further amount of aluminosilicate and to store the resulting suspension to improve the catalyst - performance (DE-OS 19821370).

After addition of the reactants in stage (d), for preparing the catalyst support is complete, the reaction mixture is stirred further for about 60 minutes and the solvent is then removed. The residue can be dried under reduced pressure, but it is preferably used further in the moist state.

The metallocene compounds, used for the supported metallocene catalyst B are prepared by reacting metallocenes of the formula IV



where L₁, L₂, F, G and R are as defined for the formula I and M' is an alkali metal, preferably lithium, with a compound of the formula V



Where M, X₁ and X₂ are as defined for the formula I and X' is a halogen atom, preferably chlorine.

Preparing the metallocene compounds B), the reaction of the dimetallated compound of the formula IV with the metal halide of the formula V can be carried out, for example, as described in EP 0 659 756. However, the reaction of the

dimetallated compound of the formula IV with the metal halide of the formula V is advantageously carried out in solvent mixtures of aromatic and/or aliphatic hydrocarbons, which may also be halogenated, with dialkyl ethers, preferably alkane/ether mixtures such as, for example, hexane/ether mixtures. Aliphatic hydrocarbons can be, for example, all C_5 - C_{12} -alkanes. Preference is given to n-pentane, n-hexane, n-heptane or cyclohexane. Among the dialkylethers, preference is given to all di- C_2 - C_4 -alkyl ethers, for example diethyl ether, di-n-propyl ether, diisopropyl ether, di-n-butyl ether or tert-butyl-methyl ether. Examples of suitable halogenated hydrocarbons are all C_1 - C_4 -chloroalkanes. Particular preference is given to dichloromethane.

The preparation of the supported metallocene catalyst according to β is carried out by suspending the catalyst support A) in an inert hydrocarbon, preferably toluene, and bringing it into contact with the metallocene compound B). In this procedure, the metallocene compound is dissolved, for example, in an inert hydrocarbon. Inert solvents which can be used are, for example, aliphatic or aromatic hydrocarbons, preferably toluene. The metallocene compounds B) are preferably used in an amount of from 0.3 wt % to 5 wt % based on the total mass of the supported catalyst. The mixing time is from 5 minutes to 24 hours, preferably from 1 to 12 hours. The mixing is carried out at a temperature of from -10 to +80°C, in particular from 20 to 70°C. The application of the metallocene compound B) is preferably carried out subsequent to the synthesis of the support A) in order to save a drying step. After the reaction is complete, the solvent is decanted and taken off under reduced pressure until a free-flowing solid remains.

Preferred monomers for the modification of the supported metallocene catalyst by pre-polymerization are 3-methylbutene-1, 4-methylhexene-1, 4-methylpentene-1, vinylcyclohexane, vinylcyclopentane and/or vinylcyclopropane.

According to the invention the pre-polymerization of the supported metallocene catalyst is carried out in absence of a solvent or in an inert hydrocarbon solvent. The pre-polymerization temperature is from particularly -20°C to 95°C , preferably from 0 to 60°C . The treatment of the supported metallocene catalyst may be carried out under reduced, atmospheric or elevated pressure batchwise or continuously.

In a preferred embodiment the monomer feed during pre-polymerization reaction is at a rate from 0.05 to 20 g monomer/g supported metallocene catalyst/h, more preferably from 0.5 to 2 g monomer/g supported metallocene catalyst/h.

According to the invention, the pre-polymerization of these monomers in presence of the supported metallocene catalyst is carried out preferably in gas phase.

In a preferred embodiment especially for liquid-phase polymerization of propylene, the modification of the supported metallocene catalyst is carried out by pre-polymerization of 4-methylpentene-1.

The modified supported metallocene catalyst of the invention is polymerization-active without further activating additives. However, it has been found to be particularly advantageous to use aluminium alkyls, preferably trimethylaluminium, triethylaluminium or triisobutylaluminium, as scavenger and as additional activator. The amount is, based on the aluminium, 50 — 5000 mol, preferably 100 — 500 mol, per mol transition metal of the metallocene compound in the modified supported metallocene catalyst.

According to the invention the modified supported metallocene catalysts may be used for the polymerization of olefins or olefin mixtures, in particular C_2 - C_{16} - α -olefins, preferably ethylene, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, cyclopentene, norbornene and/or norbornadiene. The modified sup-

ported metallocene catalysts make possible the preparation of homopolymers, copolymers and blockcopolymers. Most preferred is the use of the modified supported metallocene catalysts for the polymerization of propylene.

The invention further provides a process for preparing polyolefins by polymerization or copolymerization of olefins, wherein the polymerization catalyst used is a modified supported metallocene catalyst as according to the invention.

In liquid phase polymerization, it is possible to use inert solvents, for example, aliphatic or cycloaliphatic hydrocarbons such as pentane, hexane or cyclohexane; toluene can also be used. Preference is given to carrying out the polymerization in the liquid monomer.

If required, hydrogen is added as molecular weight regulator. The total pressure in the polymerization is usually 0.5 – 150 bar. Polymerization is preferably carried out in the pressure range of 1 – 40 bar.

In the copolymerization of ethylene with propylene, the polymerization is preferably carried out in liquid propylene or in hexane as suspension medium. In the polymerization in liquid propylene, the ethylene is preferably fed in an amount such that a partial pressure ratio $P_{\text{propylene}}/P_{\text{ethylene}} > 0.5$, in particular > 1.0 , is established over the liquid phase (P_{ethylene} = partial pressure of the ethylene in the gas phase over the suspension; $P_{\text{propylene}}$ = partial pressure of the propylene in the gas phase over the suspension). In the copolymerization in hexane as suspension medium, an ethylene/propylene gas mixture having a propylene content of from 1 to 50 mol%, preferably from 5 to 30 mol%, is fed in. The total pressure is kept constant during the polymerization by metering in a further amount. The total pressure is from 0.5 to 40 bar, preferably from 1 to 20 bar. The polymerization time is from 10 minutes to 6 hours, preferably from 30 minutes to 2 hours.

The modified supported metallocene catalysts make possible the preparation of high molecular weight polyolefins and olefin copolymers without reactor fouling, without formation of polymer fines resulting from soluble catalyst components and disrupted catalyst components in the initial phase of the olefin polymerization, especially under technical liquid polymerization conditions. Particle size and particle size distribution may be controlled in all stages of polymerization process. The polyolefins and olefin copolymers are obtained in granular form even at high polymerization conversions, they have a high bulk density and a low fines content.

The following examples illustrate the invention.

Abbreviations used are :

$^{13}\text{C-NMR}$	^{13}C nuclear magnetic resonance spectroscopy
d_{50}	Mean particle diameter determined by sieve analysis
$^1\text{H-NMR}$	^1H nuclear magnetic resonance spectroscopy
M_w	Weight average molar mass in g/mol determined by GPC
M_n	Number average molar mass in g/mol determined by GPC
M_w / M_n	Polydispersity
MAO	Methylaluminoxane
MC	Metallocene compound
MS	mass spectrometry
T_m	Melting point determined by DSC
cat_{pure}	supported catalyst without pre-polymer
$\text{cat}_{\text{pre-pol}}$	pre-polymerized catalyst
m_{cat}	weight of the supported catalyst
$m_{\text{pre-pol}}$	weight of the pre-polymer

Example 1

Preparation of the catalyst support

The silica (pore volume 1.58 cm³/g; surface area 300 m²/g) was dried at 200 °C using the procedure described in EP 787 746 Example 1. The OH content was 2.05 mmol/g SiO₂.

109.1 g of the dried oxide were suspended in 1.4 l of dry toluene in a three-neck flask equipped with a stirrer and two dropping funnels. In the first dropping funnel, 252 g (1298.3 mmol of Al) of a 30% strength solution of methylaluminoxane (MAO) in toluene were mixed with 740 ml of toluene and the second dropping funnel was charged with a solution of 12.25 g bisphenol A (53.72 mmol) in 613 ml oxygen-free toluene.

After 127.5 ml of the MAO solution had been initially introduced into the suspension at 55 °C within 15 minutes under moderate stirring, the two solutions were simultaneously added dropwise within approximately 40 minutes. The stirrer speed during this procedure was 200 rpm. The rate of dropwise addition was low and was selected such that both solutions were consumed at a suitable decrease in volume. The suspension was subsequently stirred for further three hours at 55 °C and was then allowed to stand. A fine white solid settled out. After pressurizing with 0.3 bar nitrogen, the cold suspension was stored for at least three weeks.

Subsequently the supernatant toluene was removed, the residue was again taken up two times with 800 ml toluene and washed for 15 minutes at 70°C. After separation of the white solid the supernatant washing solutions were removed. The resulting catalyst support suspension was directly used for the catalyst preparation.

Example 2

Preparation of the metallocene compound

121 ml of a 1.5 molar methyllithium solution (180.3 mmol) are added under argon at $-80\text{ }^{\circ}\text{C}$ to a solution of 47.5 g (90.2 mmol) of 1,1,1,2-tetramethylbis [2-methyl-4-phenylindenyl] disilane (M. Kumada, J. Organomet. Chem. 43 (1972) 283) in 400 ml of absolute diethyl ether. The reaction mixture is brought to room temperature over a period of 1 hour and stirred further for 20 hours at room temperature. After taking off the solvent in a high vacuum, a red-brown oily residue is obtained. This is admixed with 200 ml of absolute n-hexane, the resulting suspension is filtered under argon and the filtration residue is washed three times with absolute n-hexane. After drying for 30 minutes in a high vacuum, 46.6 g of the corresponding dilithium salt (96.0 % yield) is obtained as an orange powder which is used without further purification for the synthesis of the zirconocene dichloride.

A suspension of 21.0 g of zirconium tetrachloride in 300 ml of absolute n-hexane is added at $-80\text{ }^{\circ}\text{C}$ to a solution of 46.6 g of the dilithium salt in 300 ml of absolute diethyl ether. After warming to room temperature over a period of two hours, the mixture is stirred for 20 hours at room temperature. After taking off the solvent in a high vacuum, the solid residue is washed twice with 100 ml absolute diethyl ether. The ether fractions are collected, the solvent is evaporated to a residual volume of 100 ml and the solution is cooled to $-30\text{ }^{\circ}\text{C}$ for a few days, yielding an amorphous product which is isolated by filtration. After 3 hours drying in vacuum, a 10.0 g amount of pseudorac-methyl(trimethylsilyl)silanediy[(2-methyl-4-phenylindenyl) zirconium dichloride (16.0 % yield) is obtained. After further recrystallization from diethylether at $30\text{ }^{\circ}\text{C}$ a purity of 99 % (11.0 % yield) is reached.

$C_{36}H_{36}Si_2ZrCl_2$ (686,99 g/mol)

MS (EI, 30 eV) [m/z (%]): 687 (14)

1H -NMR (CD_2Cl_2) [ppm]: 0,62 (s, 9H, $(CH_3)_3Si-SiCH_3$) ; 1.51 (s, 3H, $(CH_3)_3Si-SiCH_3$) ; 2.26 and 2.32 (s, 3H, CH_3 -Ind) ; 6.95 to 7.62 (m, 18 H, Ph/Ind-H)

Example 3

Preparation of the supported metallocene catalyst

To 19.96 g of the catalyst support, prepared according to example 1, suspended in toluene (the solid is covered), a solution comprising 0.177 g of methyl (trimethylsilyl) silanediylbis-(2-methyl-4-phenylindenyl) zirconium dichloride, prepared according to example 2 and 60 ml of toluene was added. The suspension became orange coloured and this colour became increasingly intense during the course of the stirring phase. After 16 hours, the stirrer was switched off. The catalyst was washed 2 times and the supernatant clear solution was decanted. Removal of the solvent at 50°C under reduced pressure gave a red/orange finely divided solid. The metallocene content was 0.9 wt %.

Example 4

Propylene polymerization using the supported metallocene catalyst

A 20 l stirred reactor was, after being made inert, charged at room temperature with 6.5 kg of liquid propylene and the mixture was stirred for 15 minutes at 200 rpm.

438 mg of the supported metallocene catalyst prepared in Example 3 were placed in the catalyst feeder. Subsequently the powder was rinsed into the reactor using a further 500 g of propylene, the stirrer speed was increased to 400

rpm, the mixture was heated over a period of 12 minutes to the polymerization temperature of 70 °C and the temperature was kept constant. The reaction was stopped after two hours by flashing off the propylene. This gave 109.5 g of polypropylene with a fines content ($< 100 \mu\text{m}$) determined by sieve analysis of 3.8 % by weight. The activity was $0.25 \text{ kg/g cat}_{\text{pure}} \times 2 \text{ h}$. The polymer particles were granular ($M_w = 604 \text{ kg/mol}$; polydispersity 2.9; $T_m = 153 \text{ °C}$) and the reactor showed deposits on the stirrer, the thermocouple and the wall above the liquid phase.

Example 5

Modification of the supported metallocene catalyst by pre-polymerization

A modified thin-film evaporator was used for the pre-polymerisation. The evaporator was placed in a glove box and equipped with a powder flask that contained the catalyst powder. The system was connected with a second flask filled with oxygen and moisture free 4-methylpentene-1. 10 g of the catalyst prepared in example 3 were placed in the powder flask. The pressure was reduced to the vapour pressure of the monomer. 0.1 bar hydrogen was added. The polymerization conversion was followed by weighing the flask. After a polymerization time of one hour the weight ratio pre-polymer to catalyst ($m_{\text{pre-pol}}/m_{\text{cat}}$) was 0.4. Softening of the pre-polymer began at a temperature of 234 °C.

Example 6

Propylene polymerization using the supported metallocene catalyst

A 20 l stirred reactor was, after being made inert with nitrogen, charged at room temperature with 6.5 kg of liquid propylene, 2 l hydrogen and with a 1 molar triethylaluminum / hexane solution and the mixture was stirred for 15 minutes at 200 rpm. The triethylaluminum / hexane solution was fed in such an amount that a TEAL/Zr molar ratio of 600 was adjusted.

260 mg of the unmodified supported metallocene catalyst prepared according to Example 3 were mixed with the co-catalyst for 15 minutes. Subsequently the mixture was rinsed into the reactor using a further 500 g of propylene, the stirrer speed was increased to 400 rpm, the mixture was heated over a period of 12 minutes to the polymerization temperature of 70°C and the temperature was kept constant. The reaction was stopped after two hours by flashing off the propylene. This gave 1536 g of polypropylene with a fines content (<100 µm) determined by sieve analysis, of 8 % by weight. The activity was 0.9 kg / g cat_{pure} x 2h. The polymer particles were granular ($M_w = 345$ kg/mol; polydispersity 2.9; $T_m = 153$ °C) and the reactor showed deposits on stirrer, thermocouple and the wall above the liquid phase.

Example 7

Propylene polymerization using a 4-methylpentene-1 pre-polymerized catalyst

The polymerisation was carried out by the method described in Example 6, but using 445 mg of the pre-polymerized catalyst of Example 5.

This gave 1938 g of polypropylene with a fines content (<100 µm) determined by sieve analysis of 1.2 % by weight. The activity was 4.4 kg / g cat_{pre-pol} x 2h (6.1 kg/g cat_{pure} x 2h). The polymer particles were granular ($M_w = 324$ kg/mol; polydispersity 2.8; $T_m = 153$ °C) and the reactor showed no deposits on the internal fittings or the wall.

Example 8

Propylene polymerization using a 4-methylpentene-1 pre-polymerized catalyst

The pre-polymerization was carried out by the method described in Example 5. The weight ratio pre-polymer to catalyst ($m_{pre-pol}/m_{cat}$) was 0.8. Softening of the pre-polymer began at a temperature of 232 °C.

The polymerization reactor was charged with 295 mg of the pre-polymerized catalyst.

This gave 1663 g of polypropylene with a fines content ($< 100 \mu\text{m}$) determined by sieve analysis of 1.5 % by weight. The activity was $5.6 \text{ kg} / \text{g cat}_{\text{pre-pol}} \times 2\text{h}$ ($10.1 \text{ kg} / \text{g cat}_{\text{pure}} \times 2\text{h}$). The polymer particles were granular ($M_w = 355 \text{ kg/mol}$; polydispersity 2.8; $T_m = 152^\circ\text{C}$) and the reactor showed no deposits on the internal fittings or the wall.

Example 9

Propylene polymerization using a 3-methylbutene-1 pre-polymerized catalyst

The pre-polymerisation was carried out by the method described in Example 5. The gaseous 3-methylbutene-1 was directly fed without dilution to the pre-polymerization reactor over a period of 4 hours. No hydrogen was used. The weight ratio pre-polymer to catalyst ($m_{\text{pre-pol}}/m_{\text{cat}}$) was 0.2. Softening of the pre-polymer began at a temperature of 301°C .

The polymerisation reactor was charged with 546 mg of the pre-polymerized catalyst.

This gave 1184 g of polypropylene with a fines content ($< 100 \mu\text{m}$) determined by sieve analysis of 0.9 % by weight. The activity was $2.2 \text{ kg} / \text{g cat}_{\text{pre-pol}} \times 2\text{h}$ ($2.6 \text{ kg} / \text{g cat}_{\text{pure}} \times 2\text{h}$). The polymer particles were granular ($M_w = 336 \text{ kg/mol}$; polydispersity 2.8; $T_m = 153^\circ\text{C}$) and the reactor showed no deposits on the internal fittings or the wall.

Example 10

Propylene copolymerization using a 4-methylpentene-1 pre-polymerized catalyst

The pre-polymerization was carried out by the method described in Example 5. The weight ratio pre-polymer to catalyst ($m_{\text{pre-pol}}/m_{\text{cat}}$) was 0.8. Softening of the pre-polymer began at a temperature of 232°C .

The 20 l stirred polymerization reactor was, after being made inert, charged at room temperature with 6.5 kg of liquid propylene, 85 g ethylene, 2 l hydrogen and with a 1 molar triethylaluminum / hexane solution and the mixture was stirred 15 minutes at 200 rpm. The triethylaluminum / hexane solution was fed in such an amount that a TEAL/Zr mole ratio of 600 was adjusted.

The polymerization reactor was charged with 295 mg of the pre-polymerized catalyst.

The reaction was terminated after 30 minutes to limit the extent of conversion.

The polymerization run gave 607 g of polypropylene copolymer with a fines content ($< 100 \mu\text{m}$) determined by sieve analysis of 1.6 % by weight. The activity was $5.8 \text{ kg} / \text{g cat}_{\text{pre-pol}} \times 2\text{h}$ ($10.4 \text{ kg} / \text{g cat}_{\text{pure}} \times 2\text{h}$). The polymer particles were granular ($M_w = 280 \text{ kg/mol}$; polydispersity 2.8; $T_m = 142 \text{ }^\circ\text{C}$) and the reactor showed no deposits on the internal fittings or the wall.

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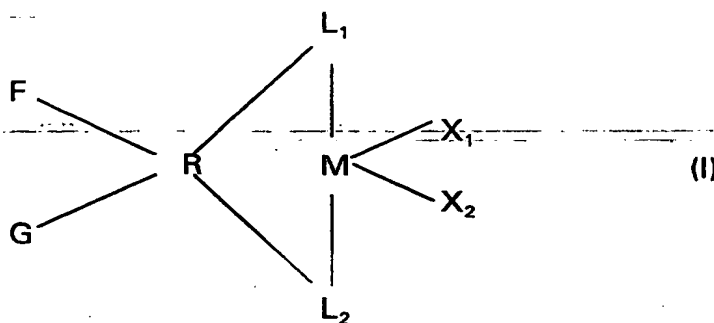
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Claims:

1. A modified supported metallocene catalyst for olefin polymerization, comprising

A) 90.0 – 99.9 parts by weight of a catalyst support based on a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture of mixed oxide thereof, which catalyst support is obtainable by simultaneous reaction with aluminoxanes and with polyfunctional organic crosslinkers,

B) 10 – 0.1 parts by weight of a metallocene compound of the formula I



where

M is a metal selected from the group consisting of Ti, Zr, Hf, V, Nb and Ta or an element selected from the group consisting of the lanthanides,

X₁ and X₂ are identical or different and are each a C₁-C₁₀-alkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₂₀-alkylaryl group, a C₇-C₂₀-arylalkyl group, a C₆-C₂₀-arylalkenyl group, hydrogen or a halogen atom,

L_1 and L_2 are identical or different and are each an unsubstituted, monosubstituted or polysubstituted monocyclic or polycyclic hydrocarbon radical containing at least one cyclopentadienyl unit which can form a sandwich structure with M,

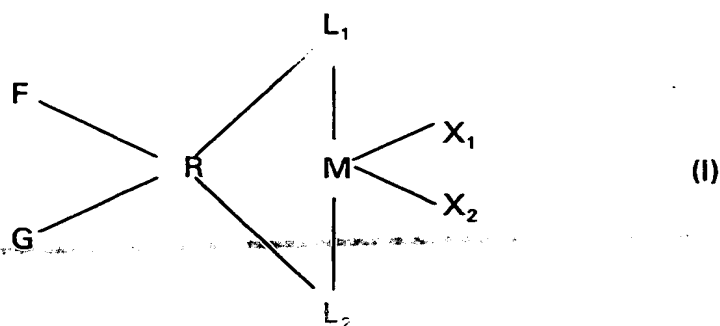
R is carbon, silicon, germanium or tin,

~~F and G are identical or different and are each a trimethylsilyl radical of the~~
formula $-\text{Si}(\text{CH}_3)_3$, where G may also be a C_1 - C_{10} -alkyl radical, preferably a C_1 - C_4 -alkyl radical, or a C_6 - C_{10} -aryl radical,

characterized in that the supported metallocene catalyst comprising A and B, has an activity of maximum 100 kg preferably maximum 50 kg, particularly preferred maximum 20 kg polyolefin/g supported catalyst/h and is modified by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization, resulting in 0.01 — 1.0 parts by weight, relative to A + B, of a polyolefin or olefin copolymer C), different to the polyolefin or olefin copolymer from the subsequent olefin polymerization or olefin copolymerization, and whereby the melting point or softening point of the polyolefin or olefin copolymer C) resulting from pre-polymerization is at least 20 °C, preferably 30 °C higher than the melting point or softening point of the polyolefin or olefin copolymer, resulting from the subsequent olefin polymerization or olefin copolymerization under application of said modified supported metallocene catalyst.

2. The modified supported metallocene catalyst as claimed in claim 1, wherein the hydrophilic inorganic oxide in the catalyst support A) is an aluminum oxide, silicon oxide, magnesium oxide, titanium oxide or zirconium oxide or a mixture or mixed oxide thereof.

3. The modified supported metallocene catalyst as claimed in claim 1 or 2, wherein the ligands L_1 and/or L_2 in the metallocene compound B) are substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl radicals.
4. The modified supported metallocene catalyst as claimed in any of claims 1 to 3, wherein the olefin or olefin mixture used in the modification of the supported metallocene catalyst by pre-polymerization, resulting a polyolefin or olefin copolymer C), is chosen from the group of 3-methylbutene-1, 4-methylhexene-1, 4-methylpentene-1, vinylcyclohexane, vinylcyclopentane and/or vinylcyclopropane.
5. A process for preparing a modified supported metallocene catalyst for polymerization of olefins, comprising the steps:
- α) preparing a catalyst support A) by
- $\alpha 1$) drying a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof at from 110 to 800°C, subsequently
- $\alpha 2$) if desired, reacting the free hydroxyl groups of the oxide completely or partially with aluminoxanes or aluminium alkyls and subsequently
- $\alpha 3$) reacting the oxide simultaneously with aluminoxanes and polyfunctional organic crosslinkers,
- β) suspending the catalyst support A) in an inert hydrocarbon and bringing it in contact with a solution of a metallocene compound B) of the formula I in an inert hydrocarbon, wherein 90.0 – 99.9 parts by weight of a catalyst support A) are mixed with 10 – 0.1 parts by weight of the metallocene compound B)



where

M is a metal selected from the group consisting of Ti, Zr, Hf, V, Nb and Ta or an element selected from the group consisting of the lanthanides,

X₁ and X₂ are identical or different and are each a C₁-C₁₀-alkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₂₀-alkylaryl group, a C₇-C₂₀-arylalkyl group, a C₈-C₂₀-arylalkenyl group, hydrogen or a halogen atom,

L₁ and L₂ are identical or different and are each an unsubstituted, monosubstituted or polysubstituted monocyclic or polycyclic hydrocarbon radical containing at least one cyclopentadienyl unit which can form a sandwich structure with M,

R is carbon, silicon, germanium or tin,

F and G are identical or different and are each a trimethylsilyl radical of the formula -Si(CH₃)₃, where G may also be a C₁-C₁₀-alkyl radical, preferably a C₁-C₄-alkyl radical, or a C₆-C₁₀-aryl radical,

γ) modifying said supported metallocene catalyst, which has an activity of maximum 100 kg preferably maximum 50 kg, particularly preferred maximum 20 kg polyolefin/g supported catalyst/h, by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization, resulting in 0.01 – 1.0 parts by weight, relative

to the sum of the weight of the catalyst support and the metallocene compound, of a polyolefin or olefin copolymer C), different to the polyolefin or olefin copolymer from the subsequent olefin polymerization or olefin copolymerization, and whereby the melting point or softening point of the polyolefin or olefin copolymer C) resulting from pre-polymerization is at least 20 °C, preferably 30 °C higher than the melting point or softening point of the polyolefin or olefin copolymer, resulting from the subsequent olefin polymerization or olefin copolymerization under application of said modified supported metallocene catalyst.

6. The process for preparing a modified supported metallocene catalyst as claimed in claim 5, characterized in that the pre-polymerization in presence of the supported metallocene catalyst is carried out in gas phase.
7. The process for preparing a modified supported metallocene catalyst as claimed in claim 5 or 6, characterized in that for liquid-phase polymerization of propylene the modification of the supported metallocene catalyst is carried out by pre-polymerization of 4-methylpentene-1.
8. A process for preparing polyolefins by polymerization or copolymerization of olefins, wherein a modified supported metallocene catalyst as claimed in any of claims 1 to 4 is contacted with the olefins.
9. The use of modified supported metallocene catalysts as claimed in any of claims 1 to 4 as polymerization catalysts for the polymerization of olefins in particular for the polymerization of propylene.

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Abstract:

A modified supported metallocene catalyst for olefin polymerization, comprising

A) 90.0 – 99.9 parts by weight of a catalyst support based on a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof, which catalyst support is obtainable by simultaneous reaction with aluminoxanes and with polyfunctional organic crosslinkers,

B) 10 – 0.1 parts by weight of a metallocene compound,

whereby the supported metallocene catalyst comprising A) and B) has an activity of maximum 100 kg, preferably maximum 50 kg, particularly preferred maximum 20 kg polyolefin/g supported catalyst/h and is modified by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization. The melting point or softening point of the polyolefin or olefin copolymer C) resulting from pre-polymerization is at least 20 °C, preferably 30 °C higher than the melting point or softening point of the polyolefin or olefin copolymer, resulting from the subsequent olefin polymerization or olefin copolymerization under application of said modified supported metallocene catalyst.

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